

Research Article

The Use of Al, Cu, and Fe in an Integrated Electrocoagulation-Ozonation Process

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This study presents the effect of supplying electrochemically generated metallic ions (Al, Cu, and Fe) during an ozonation process for treating industrial wastewater. The pollutant removal efficiencies of the electrocoagulation (EC), ozonation, and coupled EC-ozonation processes were examined by the decrease in chemical oxygen demand (COD) as a function of treatment time. The EC was performed in a raw industrial wastewater, which has contributions from 39 chemical, 34 metal finishing, 22 textile, 11 leather, and 5 automotive plants, at pH (7.3) using a current density of 150 A/m^2 for 60 min, giving a 45% reduction in COD. The ozonation process was more effective with the same wastewater, reducing the COD by 52% after 60 min of treatment. Combining the EC and ozonation methods resulted in a synergistic process that improves the reduction of COD in a shorter time. In just 12 min the integrated process reduced the COD by 88%. Thus, the combination of EC and ozonation processes improves noticeably the wastewater quality, decreasing the treatment time and also reducing the sludge production.

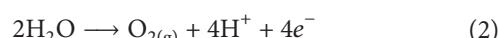
1. Introduction

Electrochemical treatment techniques are a real alternative for treating wastewater, since the system configuration is quite simple. The electrochemical cells are easy to operate and in many cases there are several reactions that take place *in situ* which minimize the chemical supply into the system. In fact, the main reagent is the electron, which is considered a clean reagent. Thus, the sludge generation is significantly reduced [1–5].

In EC the cathodic and anodic reactions are used to produce coagulants *in situ*, which destabilize the colloidal particles. In wastewater, colloidal particles are negatively charged (typically -40 to -20 mV) with the surrounding positive ions forming a double electric layer; therefore colloidal particles repel each other, preventing contact. Therefore, the main aim of this process is to destabilize the colloids using the generated *in situ* coagulants, so the particles can aggregate forming “flocs” and then these flocs precipitate and sediment and could be separated from the aqueous solution [6–10].

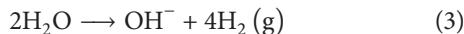
From the technological point of view, the principal variation from chemical coagulation is that the external dosing is eliminated, since the metal cations are produced *in situ*. However, there are some other advantages such that particle settling is faster and sludge generation is decreased [11–13]. Sometimes some chemicals are required, for example, a supporting electrolyte is added when the conductivity of the solution is too low.

There are two principal anodic reactions: one is related to the metal oxidation (Fe, Al, Zn, or Cu) which leads to the metal dissolution into aqueous solution (Reaction (1)) and the other one is the water oxidation (Reaction (2)):



In the case of cathodic reaction, regardless of metal, water reduction is the main reaction (Reaction (3)). The produced hydroxyl ions react in the bulk solution with metal cations

to form insoluble species, whereas the H_2 leaves the system [14–16]:



On the other hand, ozonation is a well-known technology for wastewater treatment. This process presents advantages, such as removal of color and odor and diminishing of COD and Total Organic Carbon (TOC). However, the gas-liquid phase mass transfer limits its efficiency. Ozone oxidizes organic pollutants by direct oxidation with ozone molecules or by the generation of $\cdot\text{OH}$ radicals, which are powerful oxidizing agents [17, 18].

Recently, many efforts have been made to increase the potential of EC as reliable pollutant removal technology by the synergistic combination with other treatment procedures [19–21]. Thus, the main aim of this work is to present some physicochemical aspects of the coupled EC-ozonation process; it is also demonstrated that, using this join method, the treatment time is reduced as compared with the sole application of EC or ozone.

2. Materials and Methods

2.1. Wastewater Samples. Industrial wastewater was used in the EC, ozone, and combined EC-ozonation processes. The wastewater was collected from a treatment plant, which receives water discharges of 144 different industries. The wastewater contribution is mainly by 39 chemical, 34 metal finishing, 22 textile, 11 leather, and 5 automotive plants. For the collection, a set of samples were introduced in plastic containers, labeled, and then refrigerated. Finally, they were transported to university laboratory.

2.2. Electrocoagulation Reactor. The EC process was carried out using an electrochemical reactor operating in batch mode. The reactor consists of a vessel with capacity of 1.0 L but only 0.8 L was used in all trials. The corresponding experiments were carried out with an arrangement of two parallel monopolar electrodes made of aluminum, copper or iron. Each electrode was 5.0×4.0 cm with a surface area of 20 cm^2 . For providing the current density of 150 A/m^2 a DC power source was supplied to the system as previously reported [22]. Samples were taken at regular intervals to determine COD.

2.3. Ozone Reactor. The ozonation was carried out using a 1.0 L glass reactor, although only 0.8 L of wastewater was used for the reaction. Ozone was introduced into the reactor through a porous plate situated at the reactor bottom. The ozone was generated using a flow rate of 60 mL/min and pressure of 3 psi by a Pacific Ozone Technology generator model number LAB212, 10 SCFH-AIR-STP. The ozone concentration at the inlet and outlet gas of the reactor was measured by 0.1 M potassium iodide titration method [23]. Samples were taken at regular intervals to determine COD.

2.4. Coupled Electrochemical-Ozone Process. The metal electrodes (consisting of an array of 2 parallel monopolar

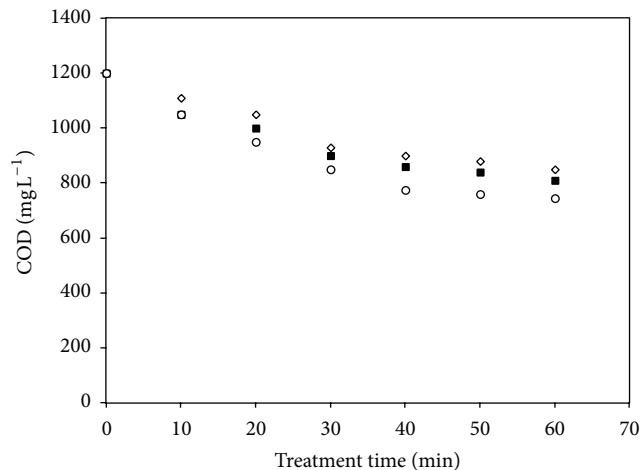


FIGURE 1: COD abatement as a function of treatment time using (◊) Al, (■) Cu, and (○) Fe anode materials. The initial pH was 7.3.

electrodes) were installed inside the ozonation reactor. The treatment was carried out using 0.8 L of wastewater. Ozone was supplied on the bottom of the reactor and the 150 A/m^2 current density for the electrodes was provided from the DC power source. Samples were taken at regular intervals to measure COD.

2.5. Methods of Analysis. The pollutant removal efficiencies of the EC, ozonation, and coupled EC-ozonation processes were determined by the reduction of COD. This parameter was determined by the open reflux method of the American Public Health Association (APHA) [23], which involves the refluxing of sample with potassium dichromate and sulfuric acid for 2 h. Prior to the test, samples were centrifuged at 10,000 rpm for 15 min to remove any suspended particles. All measurements were done in duplicate and the plotted values represent the average of the results. The estimated errors are within 2%.

2.6. Chemical Distribution Species Diagrams. In order to calculate and elaborate the aluminum, copper, and iron species diagrams as a function of pH the MEDUSA program was used [24]. These diagrams are presented in Figure 2.

3. Results and Discussion

3.1. Electrocoagulation. Figure 1 shows the COD removal as a function of EC treatment time, using three different anodes (Al, Cu, and Fe). As it is observed, the maximum removal is achieved by using Al electrodes, whereas a similar behavior is observed for Fe and Cu electrodes. EC relies on the floc formation by the *in situ* anode dissolution. The production of hydroxyl anions due to water reduction reaction in the cathode produces an increment in the pH of the solution. Both electrodic reactions result in the formation of insoluble compounds, which precipitates removing the pollutant from aqueous solution.

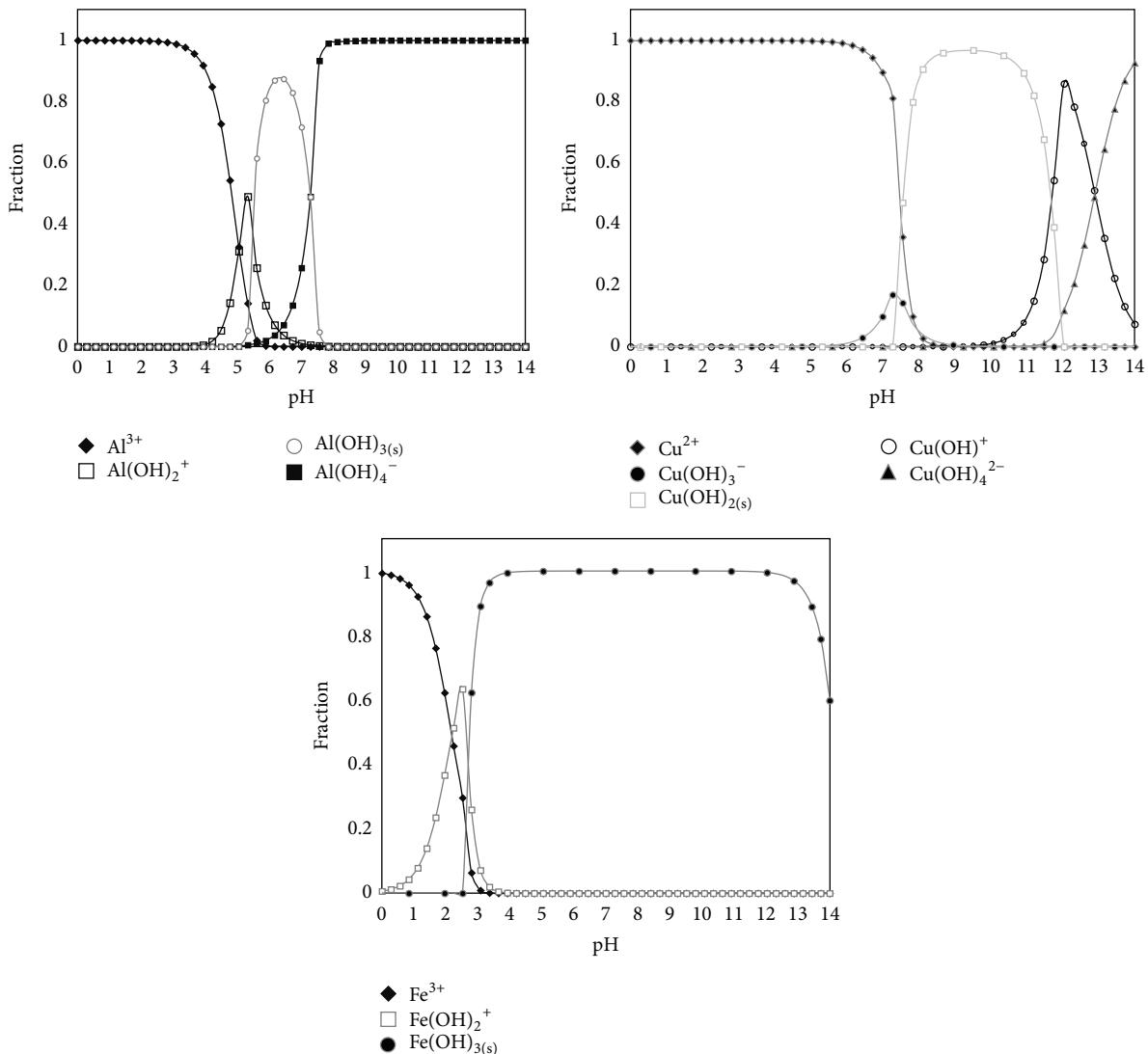


FIGURE 2: Chemical species diagram for Al, Cu, and Fe in aqueous solution as a function of pH. These diagrams were obtained using the MEDUSA program.

The chemical species distribution obtained using the MEDUSA program for the three cations is presented in Figure 2. From Figure 2 it can be observed that in the three cases at acidic conditions free cations, that is, Al³⁺, Cu²⁺, and Fe³⁺, are the predominant species. However, once the pH increases hydroxo complexes start to form and under neutral conditions the insoluble species are obtained. Note that the initial wastewater was 7.3; at this condition the Cu is still as cation, whereas the Al and Fe are already forming hydro complexes. EC removes the pollutants due to the charge neutralization of the colloids present in the system and also by pollutant attraction due to electrostatic forces to the insoluble metal species [25]. The efficiency of EC is directly related to the amount of pollutants present in wastewater [26]. However, the remaining COD present in the system indicates that there are dissolved pollutants, which cannot be removed using this method. Thus, it required a coupled system which increases the pollutant removal rate.

3.2. Ozone. The ozone effect on the COD reduction into wastewater is presented in Figure 3. As it is shown, there is only a reduction of about 50% after one hour of treatment.

The behavior in the reduction of COD can be attributed to the decomposition of ozone in water to form hydroxyl radicals, which occurs as described in [27]

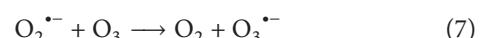
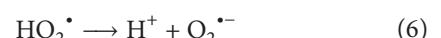
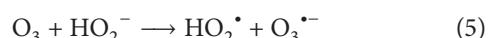


TABLE 1: Pollutant removal efficiency with a combined process is applied.

| Pollutant | Electrode type and ozone flow rate | Removal efficiency | Ref. |
|----------------------------------|---|------------------------|------|
| Distillery effluent | Iron electrodes, 15 mL O ₃ min ⁻¹ | 83% COD, 100% color | [31] |
| Industrial wastewater | Iron electrodes, 23 mL O ₃ min ⁻¹ | 63% COD, 90% turbidity | [18] |
| Boat pressure washing wastewater | Iron and aluminium electrodes, 10 mL O ₃ min ⁻¹ | 88% TOC, 76% COD | [32] |
| Reactive blue | Iron electrodes, 20 mL O ₃ min ⁻¹ | 80% TOC, 96% color | [33] |
| Reactive black | Iron electrodes, 20 mL O ₃ min ⁻¹ | 60% COD, 94% color | [34] |
| Reactive yellow | Iron electrodes, 20 mL O ₃ min ⁻¹ | 85% TOC, 100% color | [35] |

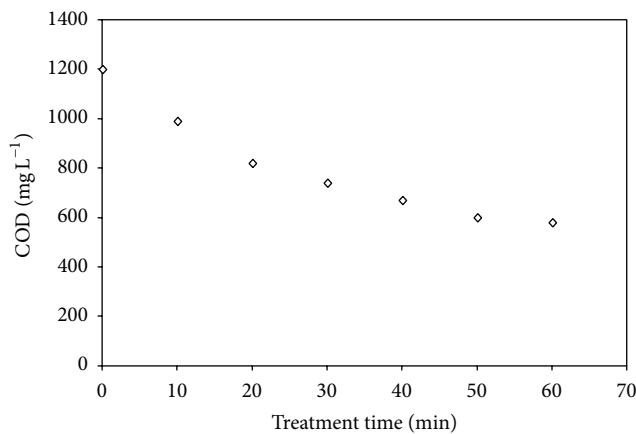


FIGURE 3: COD abatement as a function of treatment time using ozone. The initial pH was 7.3.

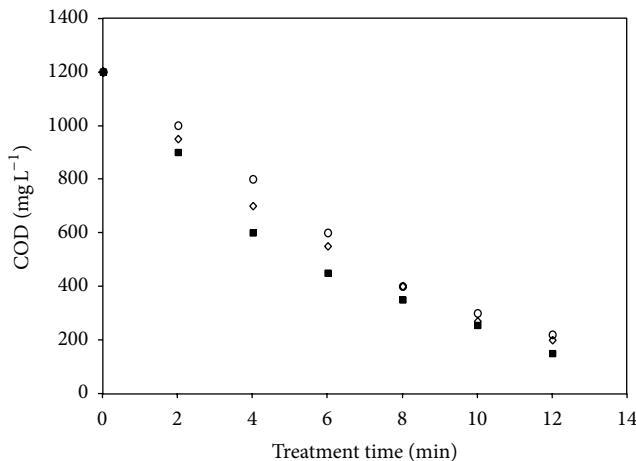


FIGURE 4: COD abatement as a function of treatment time when the coupled EC-ozonation process is used, and (◊) Fe, (■) Cu, and (○) Al anode materials are employed. The initial pH was 7.3.

It is noticeable that the generation of hydroxyl radicals is limited by the amount of ozone introduced into the system, but the mass transfer of the ozone from the gas to the liquid phase also affects this process.

3.3. Electrocoagulation-Ozonation. Figure 4 presents the pollutant removal when the coupled electrochemical-ozone is applied to wastewater. As can be observed, a faster and

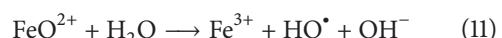
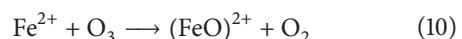
efficient removal is obtained. Since in EC the COD removal was around 45% in 60 min, using the coupled process, the pollutants decreased in about 85%, but in only 12 min. This indicates that the process speed is increased 4-fold, and the removal yield is also incremented twice.

As described previously, the dissolved metal provided by the electrochemical reactor is not enough to remove all the pollutants present in aqueous solution. Thus, the ozone contributes importantly to improving the pollutant removal. Some of the advantages of adding ozone during the EC process are the following: it provides good mixing through the reactor which improves the mass transfer, increases the oxidation of dissolved pollutants, and reduces the amount of produced sludge.

Table 1 presents recent works that describe the pollutant removal efficiency when the coupled EC-ozonation process is applied. It can be noticed that most of the studies used iron electrodes and ozone flow rate between 15 and 25 mL per min and that the color removal achieves nearly 100% in all cases. However, the COD or TOC could be reduced up to 90%.

3.4. Mechanism. In addition to the improvement coming from the addition of the effects of the separated single treatment technology, the combined process involves an increased hydroxide radical production because transition metal ions (Fe^{2+} , Mn^{2+} , Ni^{2+} , Co^{2+} , Cd^{2+} , Cu^{2+} , Ag^+ , and Zn^{2+}) work as catalysts in the homogeneous liquid phase for the degradation of organic pollutants in wastewater. During the combined process, the metal ion established the rate of reaction in the degradation system and the efficiency of ozone application.

The most accepted mechanisms for which the metal ions accelerate the decomposition of ozone to generate hydroxyl radical are shown in (10)–(12). The Fe^{2+} cation is used as example in the well-known Fenton process. This mechanism helps to explain the synergistic effect of the combination of both technologies and the resulting high efficiencies [28]:



To explain why there is no 100% of COD removal, it is necessary to remember that degradation processes that involved oxidants, despite their high reactivity and low selectivity, normally also produce refractory final products.

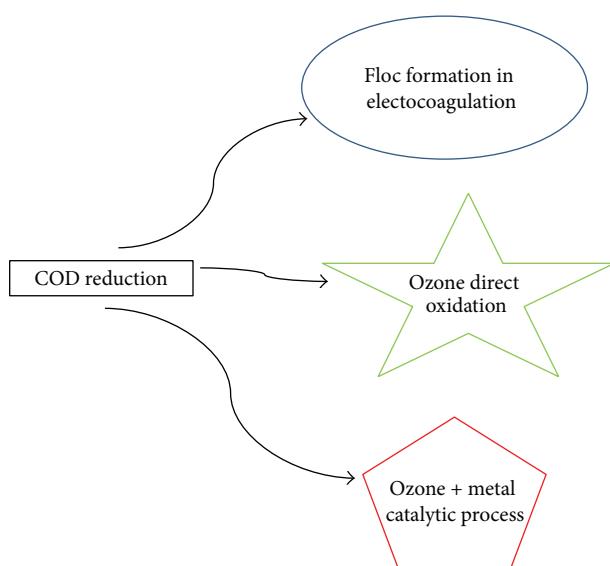


FIGURE 5: Schematic illustration of all mechanisms that takes place in the coupled EC-ozonation process.

These refractory carbon compounds are usually composed of small carboxylic acids, such as formic, succinic, oxalic, and acetic. They are refractory in nature and their final degradation in CO_2 and water could be prohibited [29].

The low molecular weight carboxylic acids could react with the hydroxyl radicals in four different ways: (a) reactions involving cleavage of the O-H bond, (b) attack by a nucleophile on the C-O bond, (c) decarboxylation, and (d) attack on R-carbon. Only the attack to the C-O bond could generate reactions that break the parent acid into compounds with lower molecular mass and finally into CO_2 and water. Several studies have shown that the oxidative refractoriness of low molecular weight aliphatic acids follows the order: acetic acid > propionic acid > formic acid > oxalic acid > glyoxylic acid [30].

Finally, Figure 5 illustrates all the mechanisms involved in the EC-ozonation process.

4. Conclusions

- EC and ozonation processes alone reduce the COD content in complex industrial wastewater up to 50% in an hour of treatment.
- Coupled electrochemical-ozone process is much more effective in a shorter period of time.
- Coupling both processes results in a synergy, which reduces the COD by 88% in only 12 min.
- There are almost no differences in the performance of coupled EC-ozonation process, regardless of the used metal cation.
- This process could have a wide application in the treatment of wastewater treatment, since it is a simple and efficient procedure. Nevertheless, an ulterior

analysis in the costs for an actual successful application is necessary.

Conflict of Interests

The authors declare that they have no conflict of interests.

Acknowledgments

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